

# Anisotropic magnetic properties of $\text{CeAg}_2\text{Ge}_2$ single crystals

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In order to investigate the anisotropic magnetic properties of  $\text{CeAg}_2\text{Ge}_2$ , we have successfully grown the single crystals, for the first time, by high temperature solution growth (flux) method. We have performed a detailed study of the grown single crystals by measuring their electrical resistivity, magnetic susceptibility, magnetization, specific heat and magnetoresistance. A clear anisotropy and an antiferromagnetic transition at  $T_N = 4.6$  K have been observed in the magnetic properties. The magnetic entropy reaches  $R \ln 4$  at 20 K indicating that the ground state and the first excited state are very closely spaced (a quasi-quartet state). From the specific heat measurements and crystalline electric field (CEF) analysis of the magnetic susceptibility, we have found the level splitting energies as 5 K and 130 K. The magnetization measurements reveal that the  $a$ -axis is the easy axis of magnetization and the saturation moment is  $\mu_s = 1.6 \mu_B/\text{Ce}$ , corroborating the previous neutron scattering measurements on a polycrystalline sample.

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## I. INTRODUCTION

In the Ce-based intermetallic compounds, the competition between the RKKY interaction and the Kondo effect leads to diverse ground states. This competition can be readily studied in the multifarious  $\text{CeT}_2\text{X}_2$  compounds, where T is a transition metal and X is a group IV element namely Si or Ge.  $\text{CeT}_2\text{X}_2$  compounds crystallize in the well known  $\text{ThCr}_2\text{Si}_2$  type tetragonal crystal structure and exhibit a wide range of interesting magnetic properties like heavy fermion superconductivity in  $\text{CeCu}_2\text{Si}_2$ <sup>1</sup>, pressure induced superconductivity in  $\text{CePd}_2\text{Si}_2$ <sup>2</sup>,  $\text{CeRh}_2\text{Si}_2$ <sup>3</sup>, unconventional metamagnetic transition in  $\text{CeRu}_2\text{Si}_2$ <sup>4</sup> etc. Similarly the isostructural germanides also show interesting magnetic properties<sup>5,6,7,8</sup>. While most of the above series of silicides and germanides have been grown in single crystalline form and the anisotropic magnetic properties have been investigated, there are no reports available on single crystalline  $\text{CeAg}_2\text{Ge}_2$  owing to the difficulty in growing the single crystal from a stoichiometric melt. Moreover, the polycrystalline data are also limited. The first report on a polycrystalline  $\text{CeAg}_2\text{Ge}_2$  was made by Rauchschalbe *et al.*<sup>9</sup> in which they have mentioned that this compound undergoes an antiferromagnetic ordering below 8 K. From neutron scattering experiments an antiferromagnetic ordering temperature of  $T_N = 7$  K was reported by Knopp *et al.*<sup>10</sup> and Loidl *et al.*<sup>11</sup>. Furthermore, an ordered moment of  $1.85 \mu_B/\text{Ce}$  at 1.5 K oriented along the [100] direction was estimated from the neutron scattering experiments. From the specific heat measurements Böhm *et al.*<sup>12</sup> have reported that  $\text{CeAg}_2\text{Ge}_2$  orders antiferromagnetically below 5 K and they observed a peak in the specific heat data at 350 mK when plotted as  $\delta C/T$  vs.  $T$  ( $\delta C = C - C_{\text{nuclear}} - C_{\text{magnon}}$ ) which they attributed to coherent electronic quasi-particles of medium heavy mass, coexisting with long range magnetic order. However, a recent report by Cordruwisch *et al.*<sup>13</sup> have re-

ported a Néel temperature of 4.5 K on a polycrystalline sample. In view of these conflicting reports on the magnetic ordering temperature and to study the magnetic properties more precisely, we have succeeded in growing a single crystal of  $\text{CeAg}_2\text{Ge}_2$  for the first time and investigated the anisotropic physical properties by means of electrical resistivity, magnetic susceptibility, magnetization, specific heat and magnetoresistance.

## II. EXPERIMENT

$\text{CeAg}_2\text{Ge}_2$  single crystals were grown by self flux method. Since the use of fourth element as flux normally introduces some inclusions in the grown single crystals, we have grown the single crystals of  $\text{CeAg}_2\text{Ge}_2$  from an off-stoichiometric melt, with excess of Ag and Ge. The binary phase diagram of Ag and Ge shows an eutectic at 650 °C. We have taken advantage of this eutectic composition and used it as a flux for the growth of  $\text{CeAg}_2\text{Ge}_2$  single crystal. Similar kind of binary eutectic compositions have been successfully used as flux for the growth of several intermetallic compounds like Au-Si binary eutectic for the crystal growth of  $\text{CeAu}_4\text{Si}_2$ <sup>14</sup>, Ag-Ge eutectic flux for the growth of  $\text{YbAgGe}$ ,<sup>15</sup> Ni-Ge eutectic composition for the growth of several  $\text{RNi}_2\text{Ge}_2$ <sup>16</sup> and Ni-B eutectic composition for the crystal growth of borocarbides<sup>17</sup>. The starting materials with 3N-Ce, 5N-Ag and 5N-Ge were taken in the ratio 1 : 16.25 : 6.75 which includes the eutectic composition of the excess flux Ag-Ge. The contents were placed in an alumina crucible, and subsequently sealed in an evacuated quartz ampoule. The temperature of the furnace was raised to 1050 °C and after homogenizing the mixture for two days, the furnace was cooled down to the eutectic temperature of the binary flux Ag-Ge over a period of 3 weeks time and then rapidly to room temperature. The crystals were separated from the flux by means of centrifuging. The

typical size of the crystal was  $6 \times 3 \times 0.3 \text{ mm}^3$ , with (001) plane as the flat plane.

The dc magnetic susceptibility and the magnetization measurements were performed in the temperature range 1.8-300 K and in magnetic fields up to 7 T along the principal directions using a Quantum Design SQUID magnetometer. The temperature dependence of electrical resistivity in the range 1.8-300 K was measured using a home made DC electrical resistivity set up. The heat capacity and magnetoresistance measurements were performed using a Quantum Design PPMS instrument in the temperature range from 0.5 K to room temperature and for fields up to 12 T.

### III. EXPERIMENTAL RESULTS

#### A. X-ray studies

Since the growth of the single crystals of  $\text{CeAg}_2\text{Ge}_2$  was performed from an off-stoichiometric starting composition we performed powder X-ray diffraction by crushing a few small pieces of the single crystals to confirm the phase purity of  $\text{CeAg}_2\text{Ge}_2$ . The powder X-ray pattern to-

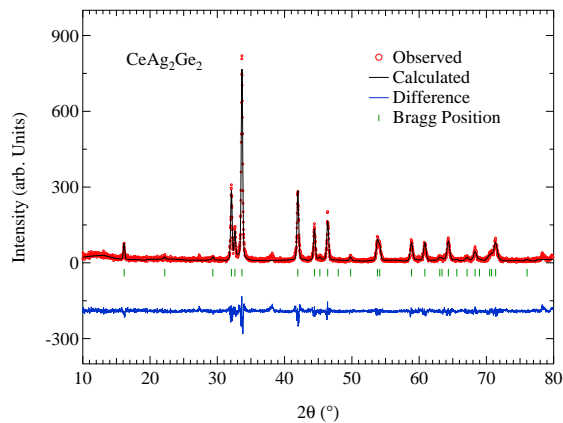


FIG. 1: (Color online) Powder X-ray diffraction pattern recorded for crushed single crystals of  $\text{CeAg}_2\text{Ge}_2$  at room temperature. The solid line through the experimental data points is the Rietveld refinement profile calculated for the tetragonal  $\text{CeAg}_2\text{Ge}_2$ .

gether with the Rietveld refinement are shown in Fig. 1. The X-ray pattern clearly reveals that the grown single crystals are single phase and no detectable traces of impurity phases are seen. From the Rietveld refinement the  $\text{ThCr}_2\text{Si}_2$ -type crystal structure of  $\text{CeAg}_2\text{Ge}_2$  is confirmed and the lattice constants were estimated to be  $a = 4.301(8) \text{ \AA}$  and  $c = 10.973(7) \text{ \AA}$ . We have also performed the energy dispersive X-ray analysis (EDAX) and confirmed the stoichiometry of  $\text{CeAg}_2\text{Ge}_2$  single crystals. The crystals were then oriented along the principal directions, namely [100] and [001] directions, by means of the Laue back reflection method. Well defined Laue diffrac-

tion spots, together with the tetragonal symmetry pattern, indicated the good quality of the single crystals. The crystals were cut along the principal direction using a spark erosion cutting machine for the anisotropic physical property measurements.

#### B. Electrical resistivity

The dc electrical resistivity of  $\text{CeAg}_2\text{Ge}_2$  in the temperature range from 1.8 to 300 K is shown in Fig. 2. The

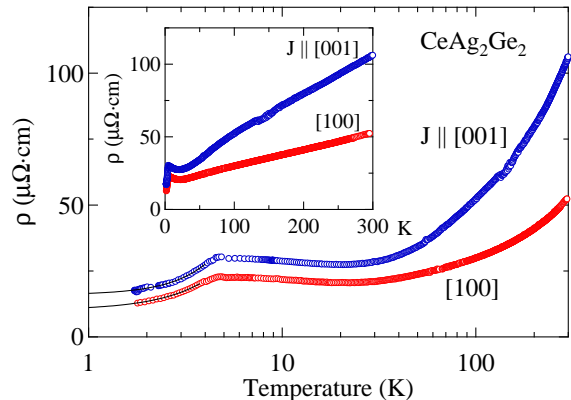


FIG. 2: (Color online) Logarithmic temperature dependence of the dc electrical resistivity of  $\text{CeAg}_2\text{Ge}_2$  for  $J \parallel [100]$  and  $[001]$ . The inset shows the linear temperature dependence of the electrical resistivity. The solid lines are least square fitting to a power law relation.

resistivity was measured for the current direction parallel to [100] and [001]. The electrical resistivity is anisotropic reflecting the tetragonal symmetry of the crystal structure. As it can be seen from the Fig. 2 the absolute value of electrical resistivity at 295 K is  $52 \mu\Omega\cdot\text{cm}$  and  $106 \mu\Omega\cdot\text{cm}$ , respectively for  $J \parallel [100]$  and  $[001]$  and at 1.8 K is  $12 \mu\Omega\cdot\text{cm}$  and  $18 \mu\Omega\cdot\text{cm}$  for  $J \parallel [100]$  and  $[001]$ , respectively. At high temperatures the scattering is phonon dominated and the resistivity decreases linearly with decreasing temperature typical of a metallic sample. The electrical resistivity shows a shallow minimum around 20 K and then increases with decrease in temperature up to 4.6 K. This increase in the electrical resistivity at low temperature can be attributed to short range antiferromagnetic order and/or the presence of weak Kondo-type interaction. It may be mentioned here that the corresponding silicide,  $\text{CeAg}_2\text{Si}_2$  has been reported to be a dense Kondo lattice antiferromagnet<sup>18</sup>. With further decrease in temperature below 4.6 K, the resistivity changes its slope and drops due to the reduction in spin-disorder scattering caused by the antiferromagnetic ordering of the magnetic moments. In the limited temperature range from 1.8 - 4.0 K the resistivity follows a power law relation  $\rho = \rho_0 + AT^n$  with  $\rho_0 = 10.15 \mu\Omega\cdot\text{cm}$ ,  $A = 0.99 \mu\Omega\cdot\text{cm}/\text{K}^{1.75}$  and  $n = 1.75$  and

$\rho_0 = 15.97 \mu\Omega\cdot\text{cm}$ ,  $A = 0.53 \mu\Omega\cdot\text{cm}/\text{K}^{2.21}$  and  $n = 2.21$  for the currents along  $J \parallel [100]$  and  $[001]$  directions, respectively. Here the exponent  $n$  is close to 2 which can in principle be explained on the basis of electron-electron scattering. Since our data do not extend for  $T \ll T_N$  we have not attempted to fit our data using sophisticated model of spin-waves.

### C. Magnetic susceptibility and magnetization

The temperature dependence of magnetic susceptibility in the temperature range from 1.8 to 300 K measured in a field of 1 kOe along the two principal directions viz.,

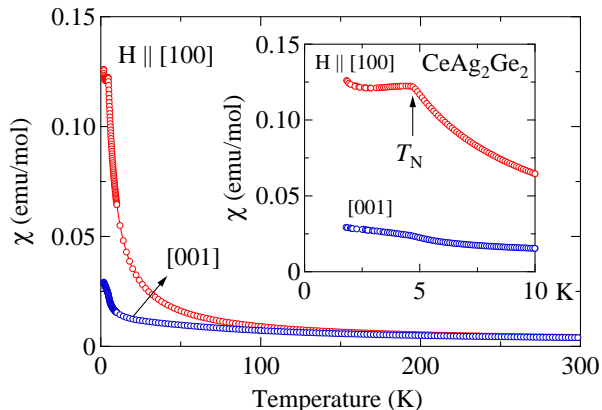


FIG. 3: (Color online) Temperature dependence of magnetic susceptibility  $\chi$  from 1.8 – 300 K. The inset shows the low temperature magnetic susceptibility.

$H$  parallel to  $[100]$  and  $[001]$  is shown in Fig. 3. The antiferromagnetic ordering at  $T_N = 4.6$  K is clearly seen as indicated by the arrow. The susceptibility below  $T_N$  remains almost  $T$ -independent and at the lowest temperature measured there is a small rise in the susceptibility, indicating that the antiferromagnetism observed in  $\text{CeAg}_2\text{Ge}_2$  is not a simple two sublattice antiferromagnetism. For example, canted antiferromagnetism may show a weak residual ferromagnetic magnetization in the Néel state. Also, this type of temperature independent susceptibility at low temperature may be attributed to the crystalline electric field (CEF) effect. The inverse magnetic susceptibility of  $\text{CeAg}_2\text{Ge}_2$  does not obey the simple Curie-Weiss law (not shown here), on the other hand, it can be very well fitted to a modified Curie-Weiss law which is given by  $\chi = \chi_0 + \frac{C}{T - \theta_p}$ , where  $\chi_0$  is the temperature-independent part of the magnetic susceptibility and  $C$  is the Curie constant. The main contributions to  $\chi_0$  includes the core-electron diamagnetism, and the susceptibility of the conduction electrons. The details of the inverse magnetic susceptibility is discussed later in the discussion part. For an effective magnetic moment of  $2.54 \mu_B/\text{Ce}$  we have estimated the  $\theta_p$  values as  $-7.2$  K and  $-42$  K for  $H \parallel [100]$  and  $[001]$ , respectively.

The field dependence of isothermal magnetization at  $T = 2$  K measured in a SQUID magnetometer up to a field of 70 kOe is shown in Fig. 4. The magnetization

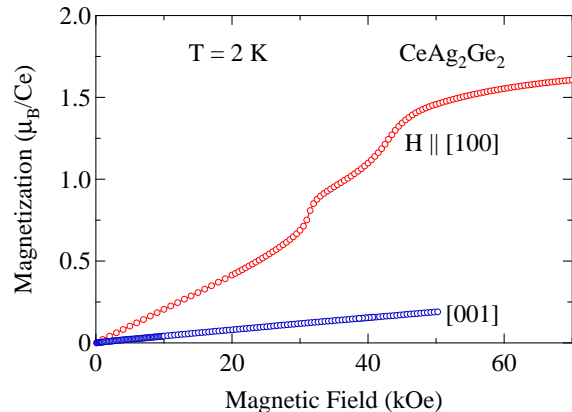


FIG. 4: (Color online) Isothermal magnetization curves of  $\text{CeAg}_2\text{Ge}_2$  measured at  $T = 2$  K along the two principal directions.

curves show large uniaxial magnetocrystalline anisotropy. The magnetization for  $H \parallel [100]$  is linear for low fields and shows metamagnetic transitions at critical fields  $H_{m1} = 31$  kOe and at  $H_{m2} = 44.7$  kOe and nearly saturates at 70 kOe with a saturation moment  $\mu_s = 1.6 \mu_B/\text{Ce}$ , this indicates that  $[100]$ -axis is the easy axis of magnetization. Here, the saturation moment is smaller than the free ion value of  $2.1 \mu_B/\text{Ce}$  which could be attributed to the crystal field effects. However, one can achieve the saturation value at high applied magnetic fields. On the other hand, the magnetization for  $H \parallel [001]$  is very small and varies linearly with field reaching a value of  $0.32 \mu_B/\text{Ce}$  at 50 kOe, indicating a hard axis of magnetization. We have also performed the isothermal magnetization at 3 K, 4 K, 5 K and 10 K for  $H \parallel [100]$ . From the differential plots of the isothermal magnetization measurements, we have constructed the magnetic phase diagram as shown in Fig. 5. The two metamagnetic transitions are clearly seen for 2 K and 3 K magnetization curves; however at 3 K only one metamagnetic transition is seen. For temperatures above the magnetic ordering temperature the magnetization curves did not show any metamagnetic behaviour and the magnetization curves were linear indicating a paramagnetic state.

### D. Specific heat

Figure 6(a) shows the temperature dependence of the specific heat of single crystalline  $\text{CeAg}_2\text{Ge}_2$  together with the specific heat of a polycrystalline reference sample  $\text{LaAg}_2\text{Ge}_2$ . The low temperature data ( $\sim 1.5$  to  $\sim 10$  K) of  $\text{LaAg}_2\text{Ge}_2$  have been fitted to the expression  $C = \gamma T + \beta T^3$  where  $\gamma$  is the electronic contribution

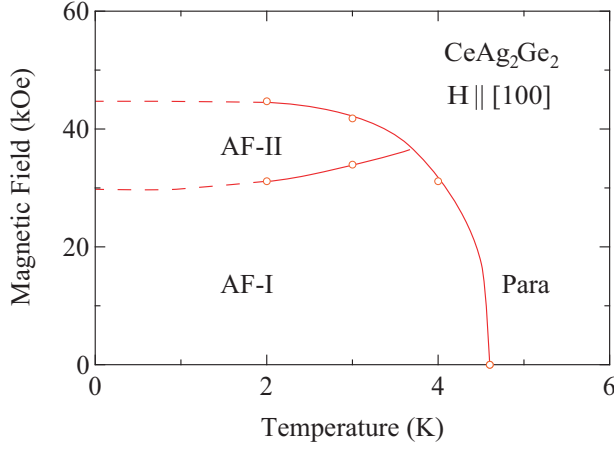


FIG. 5: (Color online) Magnetic phase diagram of  $\text{CeAg}_2\text{Ge}_2$  for  $H \parallel [100]$ .

and  $\beta$  is the phonon contribution to the heat capacity. The  $\gamma$  and  $\beta$  values thus obtained are estimated to be  $2.8 \text{ mJ/K}^2\cdot\text{mol}$  and  $0.59 \text{ mJ/K}^4\cdot\text{mol}$ , respectively. The inset of Fig. 6(a) shows the low temperature part of the specific heat and the antiferromagnetic ordering is manifested by the clear jump in the specific heat at  $T_N = 4.6 \text{ K}$  as indicated by the arrow. The inset of Fig. 6(b) shows the specific heat in the form of  $C/T$  versus  $T$ . Just below the magnetic ordering the specific heat shows a broad peak in the  $C/T$  versus  $T$  curve which presumably indicates the presence of low lying crystal field levels. Assuming the lattice heat capacity of  $\text{CeAg}_2\text{Ge}_2$  is the same as that of  $\text{LaAg}_2\text{Ge}_2$ , the  $4f$ -derived contribution to the heat capacity  $C_{\text{mag}}$  was obtained by subtracting the specific heat of  $\text{LaAg}_2\text{Ge}_2$  from the total specific heat of  $\text{CeAg}_2\text{Ge}_2$ . Figure 6(c) shows  $C_{\text{mag}}/T$  versus  $T$  together with the entropy  $S_{\text{mag}}$  which is obtained by integrating  $C_{\text{mag}}/T$ . As it can be seen from the figure, the entropy of  $\text{CeAg}_2\text{Ge}_2$  is very high at the magnetic ordering temperature and reaches  $R \ln 4$  near  $20 \text{ K}$ . In tetragonal symmetry, the degenerate six fold levels of the ground-state multiplet of  $\text{Ce}^{3+}$  split into three doublets and  $\Delta_1$  and  $\Delta_2$  are the excitation energies of the first and second excited states, respectively. Since the entropy change reaches  $R \ln 4$ , not too far above  $T_N$ , one can come to a conclusion that the ground state and the first excited state are very closely spaced or nearly degenerate. This finding clearly corroborates the earlier neutron scattering results by Loidl *et al.*<sup>11</sup> in which they could observe only one crystal field transition at  $11 \text{ meV}$  and concluded that the ground state is almost degenerate with the first excited state.

From the crystalline electric field analysis of the magnetic susceptibility data, to be discussed later, we found that the energies of the excited states  $\Delta_1$  and  $\Delta_2$  as  $5 \text{ K}$  and  $130 \text{ K}$ , respectively. Due to the very small splitting energy between the ground state and the first excited state the estimation of the Sommerfeld coefficient  $\gamma$ , by the usual method, from the low temperature data will

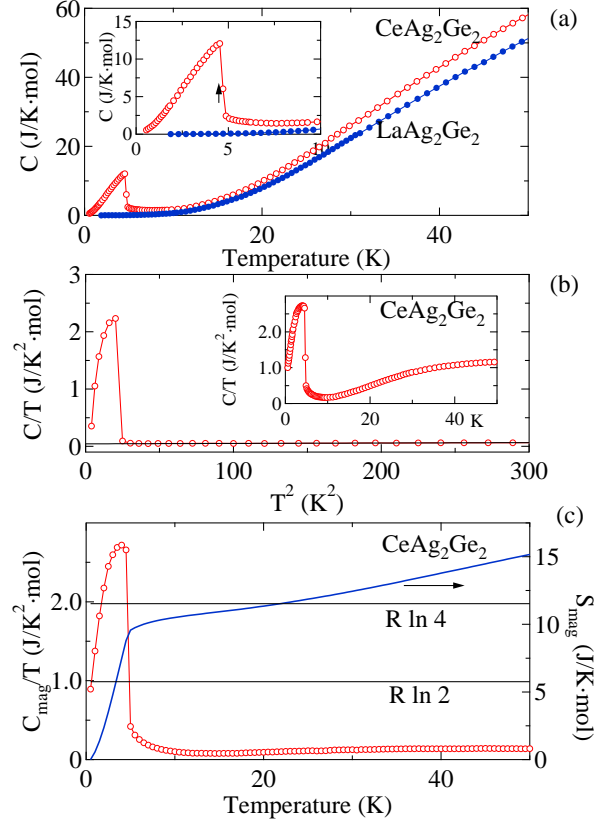


FIG. 6: (Color online)(a) Temperature dependence of the specific heat of  $\text{CeAg}_2\text{Ge}_2$  and  $\text{LaAg}_2\text{Ge}_2$ , the inset shows the low temperature part, (b) specific heat of  $\text{CeAg}_2\text{Ge}_2$  in the form of  $C/T$  vs.  $T^2$  after subtracting the schottky and the  $4f$  contribution, the solid line shows the extrapolation of the high temperature specific heat to  $0 \text{ K}$ , inset shows  $C/T$  versus  $T$  and (c) magnetic specific heat  $C_{\text{mag}}$  in the form of  $C_{\text{mag}}/T$  vs.  $T$  together with the magnetic entropy  $S_{\text{mag}}$ .

lead to ambiguity. Hence we estimated the  $\gamma$  value from the high temperature data in the paramagnetic region above the magnetic ordering after subtracting the Schottky contribution and linearly extrapolating the  $C/T$  versus  $T^2$  behaviour to  $T = 0 \text{ K}$  and is shown in Fig. 6(b). The  $\gamma$  value thus estimated is  $45 \text{ mJ/K}^2\cdot\text{mol}$ .

### E. Magnetoresistance

We have also studied the effect of magnetic field on the resistivity of  $\text{CeAg}_2\text{Ge}_2$ . The magnetic field did not have any appreciable effect on the resistivity for the field perpendicular to the easy axis direction. On the other hand, when the field was applied parallel to the easy axis direction, we found that the resistivity gradually decreased with increasing field. In Fig. 7 we have plotted the normalized magnetoresistance  $\Delta\rho/\rho_0 = [\rho(B) - \rho(B = 0)]/\rho(B = 0)$  as a function of applied magnetic field at various fixed temperatures. With increasing

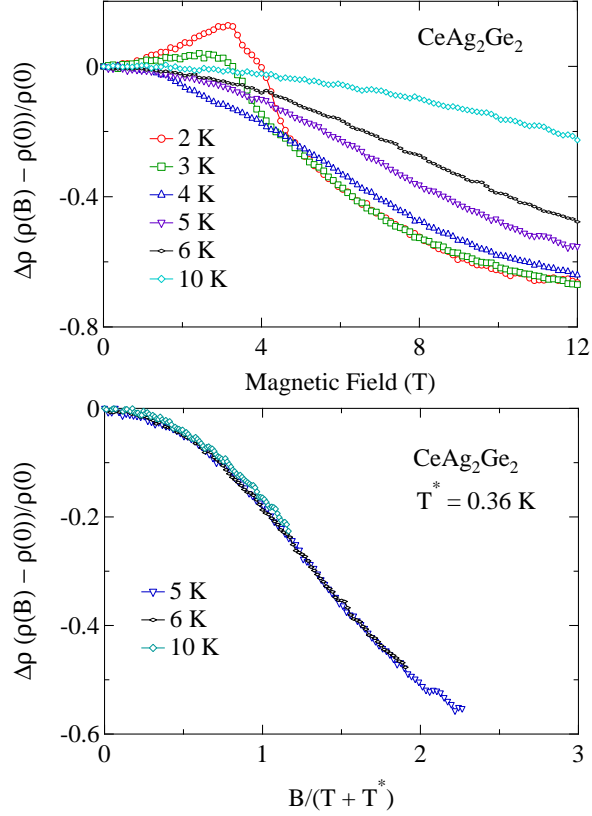


FIG. 7: (Color online) (a) Isothermal normalized magnetoresistance for  $\text{CeAg}_2\text{Ge}_2$  as function of applied magnetic field for  $J \parallel [100]$  and  $H \parallel [100]$ . (b) Normalized magnetoresistance, in the paramagnetic state, plotted as a function of  $B/(T + T^*)$ .

magnetic field for  $H \parallel [100]$ ,  $\Delta\rho/\rho_0$  at 2 K initially increases in the positive direction and then turns negative at higher magnetic fields, giving rise to a maximum at 3.1 T. This field value coincides with the metamagnetic transition observed in the magnetization measurement at  $T = 2$  K. Such a behaviour of the magnetoresistance is qualitatively consistent with the theoretical calculation given by Yamada and Takada<sup>19</sup>. In the antiferromagnetic state ( $H < H_m$ ), the magnetic moment fluctuation in one magnetic sublattice is enhanced by the field while, in the field induced ferromagnetic state ( $H > H_m$ ), the fluctuation is suppressed by the field. The change in the fluctuation is reflected in the magnetoresistance. With the increase in the temperature, the peak in the magnetoresistance moves toward lower fields and decreases, finally disappears for temperatures above  $T_N$ . In the paramagnetic region the negative magnetoresistance is due to the freezing out of the spin-flip scattering by the magnetic field. The normalized magnetoresistance for  $T > T_N$  can be mapped onto a single curve using the scaling relation  $\Delta\rho/\rho(0) = f[B/(T + T^*)]$  derived by Schlottmann<sup>20</sup> within the Bethe-ansatz approach, as shown in Fig. 7(b). Here  $T^*$  is the characteristic temperature which is an ap-

proximate measure of the Kondo temperature  $T_K$  and is estimated to be 0.36 K. This indicates that the Kondo effect is very weak in  $\text{CeAg}_2\text{Ge}_2$ , which substantiates our earlier prediction from the zero field resistivity data.

#### IV. DISCUSSION

From the results of the electrical resistivity, susceptibility and specific heat measurements it can be clearly seen that  $\text{CeAg}_2\text{Ge}_2$  undergoes an antiferromagnetic ordering at 4.6 K with the easy axis of magnetization as  $[100]$ . The magnetization at 70 kOe reaches  $1.6 \mu_B/\text{Ce}$  thus corroborating the earlier neutron scattering experiment<sup>11</sup> on a polycrystalline sample of  $\text{CeAg}_2\text{Ge}_2$ . The electrical resistivity at high temperature shows a typical metallic behaviour and at sufficiently low temperature it shows a weak minimum before ordering magnetically. This behaviour is quite different from what one has observed in the  $\text{CeCu}_2\text{Ge}_2$  which is similar to  $\text{CeAg}_2\text{Ge}_2$  both structurally and magnetically, although the antiferromagnetic ordering temperature is nearly equal ( $T_N = 4.1$  K for  $\text{CeCu}_2\text{Ge}_2$  and  $T_N = 4.6$  K for  $\text{CeAg}_2\text{Ge}_2$ ). The logarithmic temperature dependence of electrical resistivity in  $\text{CeCu}_2\text{Ge}_2$  exhibit a double peak structure which is presumably attributed to the combined influence of the Kondo and crystalline electric field (CEF) effects. The Kondo temperature of  $\text{CeCu}_2\text{Ge}_2$  was estimated to be about 6 K<sup>21</sup>, whereas for  $\text{CeAg}_2\text{Ge}_2$  the Kondo temperature is very small. Since the unit cell volume of  $\text{CeCu}_2\text{Ge}_2$  is smaller ( $V \approx 178 \text{ \AA}^3$ ), a larger value of the Kondo coupling constant  $J_{sf}$  is expected and hence the Kondo interaction dominates in  $\text{CeCu}_2\text{Ge}_2$  compared to that in  $\text{CeAg}_2\text{Ge}_2$  ( $V \approx 203 \text{ \AA}^3$ ). In  $\text{CeCu}_2\text{Ge}_2$  superconductivity occurs when the unit cell volume attains a favourable value of  $168 \pm 3 \text{ \AA}^3$ . This is achieved with an external pressure of 7 GPa. Considering this fact the unit cell volume of  $\text{CeAg}_2\text{Ge}_2$  is quite large and one would require a very high pressure to reduce the unit cell volume to nearly  $168 \pm 3 \text{ \AA}^3$  for probable observation of superconductivity. Based on this it can be said that  $\text{CeAg}_2\text{Ge}_2$  lies on the left hand side of the Doniach phase diagram in which the RKKY energy scale is dominant and Kondo interaction is weak.

The heat capacity measurement of  $\text{CeAg}_2\text{Ge}_2$  single crystal clearly reveals the presence of low lying crystal field levels with a very small separation between the ground state and the first excited state indicating that the ground state is a quasi-quartet state instead of a doublet which is usually observed for a tetragonal site symmetry. In order to further analyze the crystal field levels and to understand the present anisotropy in the magnetic susceptibility we have performed the CEF analysis on the susceptibility data. For the purpose of CEF analysis in Fig. 8 we have plotted the experimental results on susceptibility in the form of  $1/(\chi - \chi_0)$ , where  $\chi_0$  was determined as  $1.33 \times 10^{-3}$  and  $1.41 \times 10^{-3} \text{ emu/mol}$  for  $H \parallel [001]$  and  $[100]$ , respectively, so an effective magnetic



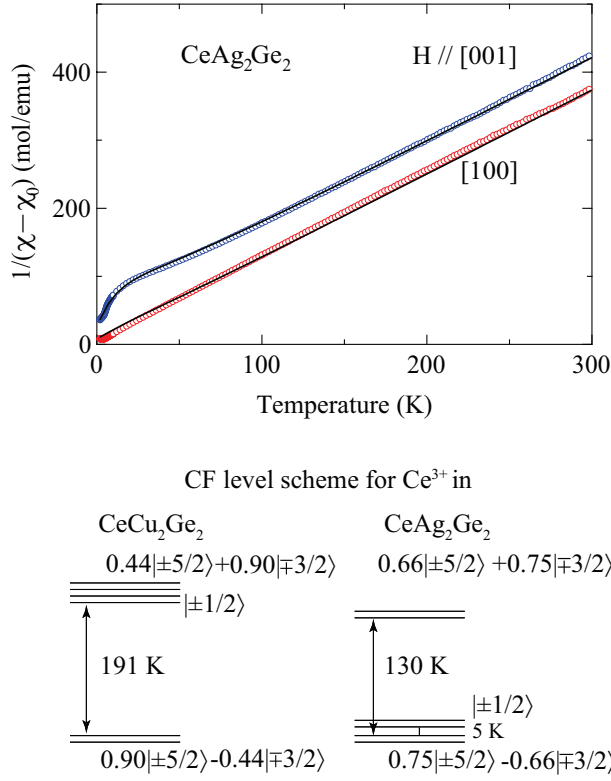


FIG. 8: (Color online) Temperature dependence of the inverse magnetic susceptibility in  $\text{CeAg}_2\text{Ge}_2$ . Solid lines are fitting to the CEF level scheme with a molecular field term. The bottom figure shows the crystal-field level scheme of  $\text{Ce}^{3+}$  in the  $\text{CeCu}_2\text{Ge}_2$  (taken from Ref.21) and  $\text{CeAg}_2\text{Ge}_2$ .

moment of  $2.54 \mu_B/\text{Ce}$  is obtained above 100 K. Similar kind of treatment has been made for  $\text{CePt}_3\text{Si}^{22}$  while performing the CEF analysis. The Ce atoms in  $\text{CeAg}_2\text{Ge}_2$  occupy the  $2a$  Wyckoff position with the point symmetry  $4/\text{mmm}$  ( $D_{4h}$ ) and hence possess the tetragonal site symmetry. The CEF hamiltonian for a tetragonal site symmetry is given by,

$$\mathcal{H}_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^4 O_6^4, \quad (1)$$

where  $B_\ell^m$  and  $O_\ell^m$  are the CEF parameters and the Stevens operators, respectively<sup>23,24</sup>. For Ce atom, the 6th order terms  $O_6^0$  and  $O_6^4$  vanishes and hence CEF Hamiltonian reduces to,

$$\mathcal{H}_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4, \quad (2)$$

The magnetic susceptibility including the molecular field contribution  $\lambda$  is given by

$$\chi^{-1} = \chi_{\text{CEF}}^{-1} - \lambda, \quad (3)$$

where  $\chi_{\text{CEF}}$  is the CEF susceptibility. Diagonalization of the CEF Hamiltonian gives us the eigenvalues and eigenfunctions. For  $\text{Ce}^{3+}$   $J = 5/2$  wave function splits into three doublets,  $\Gamma_7^{(1)} = a|\pm 5/2\rangle + b|\mp 3/2\rangle$ ,  $\Gamma_7^{(2)} = a|\pm 3/2\rangle - b|\mp 5/2\rangle$  and  $\Gamma_6 = |\pm 1/2\rangle$ , where  $a$  and  $b$  are mixing parameters with the condition  $a^2 + b^2 = 1$ . The CEF parameters were estimated from the fits to the magnetic susceptibility. Solid lines in Fig. 8 show the least square fitting to Eqn. 3, the CEF parameters thus obtained are listed in Table I. The corresponding crystal field level scheme together with that of  $\text{CeCu}_2\text{Ge}_2$  is shown in the bottom part of Fig. 8. The crystal field level scheme for  $\text{CeCu}_2\text{Ge}_2$  is taken from Ref. 21. The ground state of  $\text{CeAg}_2\text{Ge}_2$  shows a mixing of  $|\mp 3/2\rangle$  and  $|\pm 5/2\rangle$  wave functions. From Fig. 8 it is obvious that the present set of CEF parameters gives a good fit to the experimental data there by explaining the anisotropy in the magnetic susceptibility. The CEF parameters have resulted in the first and second excited states at  $\Delta_1 = 5$  K and  $\Delta_2 = 130$  K. It is interesting to note here that the CEF level scheme of  $\text{CeCu}_2\text{Ge}_2$  is qualitatively opposite to the present case where the ground state is a doublet and the first and second excited states are nearly degenerate. This can be explained on the basis of the sign of the  $B_2^0$  parameter. For  $\text{CeCu}_2\text{Ge}_2$  it is negative while it is positive for  $\text{CeAg}_2\text{Ge}_2$ . This change in sign of  $B_2^0$  suggests that the CEF potential in  $\text{CeT}_2\text{Ge}_2$  is largely dependent on the hybridization between localized  $f$ -electron states and the conduction-electron bands.

## V. CONCLUSION

Single crystals of  $\text{CeAg}_2\text{Ge}_2$  have been grown for the first time, by flux method by using a Ag-Ge binary eutectic composition as flux. The antiferromagnetic ordering temperature  $T_N = 4.6$  K is clearly manifested by the resistivity, heat capacity and susceptibility measurements. Thus the ambiguity about the magnetic ordering temperature of this compound, reflected in the conflicting reports earlier in the literature, has been removed. A large anisotropy in the electrical resistivity, magnetic susceptibility and magnetization is observed. The susceptibility and magnetization clearly reveals that [100]-axis as the easy axis of magnetization with a moment of  $1.6 \mu_B/\text{Ce}$  at 70 kOe. Metamagnetic transitions have been observed at the critical fields,  $H_{m1} = 31$  kOe and at  $H_{m2} = 44.7$  kOe. The heat capacity and the susceptibility data clearly support the closely spaced ground and first excited states, which have been analyzed by the CEF calculations.

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TABLE I: CEF parameters, energy level schemes and the corresponding wave functions for CeAg<sub>2</sub>Ge<sub>2</sub>.

CEF parameters						
	$B_2^0$ (K)	$B_4^0$ (K)	$B_4^4$ (K)	$\lambda_i$ (emu/mol) <sup>-1</sup>		
	2.24	-0.19	2.40	$\lambda_{[100]} = -7.2$		
				$\lambda_{[001]} = -26$		
energy levels and wave functions						
$E$ (K)	$ +5/2\rangle$	$ +3/2\rangle$	$ +1/2\rangle$	$ -1/2\rangle$	$ -3/2\rangle$	$ -5/2\rangle$
130	-0.656	0	0	0	-0.754	0
130	0	-0.754	0	0	0	-0.656
5	0	0	0	1	0	0
5	0	0	1	0	0	0
0	0	-0.656	0	0	0	0.754
0	0.754	0	0	0	-0.6565	0

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